STUDY OF CORROSION INHIBITORS RELEVANT TO REFINERY INDUSTRY

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DEDICATED

TO

CHERISHED FEET OF SHRI SAI BABA

&

MY LOVING PARENTS

DEPARTMENT OF APPLIED CHEMISTRY
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CERTIFICATE

It is to certify that this dissertation entitled **"Study of corrosion inhibitors relevant to refinery Industry"**, submitted by **Ms Nidhi Saxena** is a record of the candidate's own work carried out by her under my supervision and guidance. The results presented in this dissertation have not been submitted elsewhere and are suitable for the submission to the award of **M.Phil degree.**

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Nidhi Saxena

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Chapter-1

Introduction

Corrosion in Refinery Industry

Corrosion problems are encountered in many refinery steps and may lead to unsafe conditions of plant and personnel. Refineries deals with various corrosion mechanism rights from atmospheric corrosion in coastal refineries to severe napthenic acid corrosion in high temperature and high velocity areas.

Corrosion mechanism may appear to be simple however lapses in close monitoring on day to day basis have resulted in catastrophic failures of plant and equipments .For a refinery the hazards of corrosion have much higher importance than the cost of corrosion.

Corrosion due to hydrochloric acid in crude and vacuum units represents a significant portion of refining cost as a result of lost production, inefficient operations, and high maintenance and corrosion control chemical costs. It also plays an important role in a petrochemical industry such as butane isomerization, ethylbenzene production and polybutene production etc. In these processes aluminium chloride and other metal chlorides are used as a catalyst. These catalysts hydrolyze to hydrochloric acid if traces of water enter with feedstocks. Corrosion in crude and vaccum units comes primarily from chlorides. Chloride corrosion is caused by hydrogen chloride, which is formed from hydrolysis of the chloride salts contained in the crude. These inorganic salts are present in crude oil from produced formation water or from contamination by seawater during shipping. The majority of the chloride salts present are magnesium, calcium and sodium salts. Sodium chloride is thermally and hydrolytically stables to about 700 K and does not significantly contribute to hydrogen chloride release. However, hydrolysis of calcium chloride and magnesium chloride is significant and begins at the temperature above 394°K and accelerate at temperature above 449-477 °K. The released hydrogen chloride is relatively non-corrosive in the vapour phase, however, below the due point of water, hydrogen chloride forms in acidic solution and become very corrosive to many common materials of construction.

One method of combating chloride corrosion is to approach strictly from a material of construction point of view. Possible materials of constructions include alloy 400, titanium, nickel alloys or some of the newer super austenitic stainless steel. However, this approach is very situation specific and may be cost prohibitive also the presence of other corrosive contaminants may render some of these materials unsuitable.

Alternatively the more cost effective methods can be the use of corrosion inhibitor with less expensive material of construction and accordingly a literature review has been carried out to study the availability of suitable inhibitor for hydrochloric acid environment.

Walker (1984) discussed factors that affect corrosion in fluid catalytic cracking unit (FCC) vapour recovery units, methods for monitoring it & using chemical inhibitors to reduce it [1]. Granese & Rosales (1987) elucidated the mechanism of corrosion inhibition of iron & steel in HCl media & concluded that inhibitors effective mainly belong to the group of nitrogen containing compounds such as alkyl & aryl amines, saturated and unsaturated N-ring compounds [2]

Jayaramanet.al (1991) perform studies to generate corrosion rate data for different crudes & study corrosion inhibiting behavior of various known amines & amino amides from non –edible oils [3]. Mehta (1992) discussed in detail the aspects of developing fatty amines or diamines as corrosion inhibitors which are widely used [4].

Granes & co workers (1992) studied various heterocyclic N-compounds in HCl by electrochemical & surface analysis & inferred that efficiency of these compound increases with number of aromatic systems and electrons availability in the molecule [5].

Quraishi et.al (1993) investigated inhibitive action of 4 amino-5 mercapto 3 methyl -1,2,4-trizole on corrosion of mild steel in 1 N H_2SO_4 & 1N HCl by potentiodynamic polarization, A C impedance & hydrogen permeation method & inhibitor is found to be very effective in bringing down the permeation current considerably in both the acid solutions [6]. Quraishi et.al (1993) have synthesized a few anils by condensing 3 alkyl 4 amino -5 mercapto 1, 2, 4 triazoles to investigate inhibitive action of

these compound on corrosion of mild steel in acidic solution & found that these entire compound show better performance [7]. Kane et.al (1993) simulated chemical process corrosion in the laboratory. They found that testing used intelligently could give significant information to support analysis, troubleshooting and materials selection [8].

Keera et.al (1994) carried out an experimental study for the measurement of corrosion at carbon steel during distillation process and they used ammonia & chlorinated hexadecyl amine inhibitor, hetrocyclic compounds Napthyl, 1,2,4 triazole-3-thione Benzy1,2,4 triazole -3-thione, on corrosion of carbon steel, Benzyl triazole is more effective than napthyl one. They found that the corrosivities of C-steel metal in the vapour phase is higher than those in the liquids phase. H_2S is not only corrodent present; HCl and volatile acid are other important factors [9].

Ajmal et al (1994) studied the inhibitive action of 2-hydrazino 6-methyl 1-benzothiazole on corrosion on mild steel in acidic solutions. They found that this compound act as a mixed inhibitor in 1N H_2SO_4 and behave predominantly as cathodic inhibitor in 1N HCl. They have also found that the inhibitive effectively inhibits permeation of hydrogen through mild steel [10].

Kane and Cayard (1995) carried out the systematic study of the various refining operating process and recommended few suggestion to improve corrosion control when processing high sulphur feedstocks [11].

A new class of acid corrosion inhibitor viz azathiones were synthesized by Quraishi et al (1995). The inhibitive action of these compounds was studied on corrosion of mild steel and in 1N HCl and 1N H_2SO_4 by both weight loss and electro chemical techniques. The authors have found that the inhibiting action of the azathiones depends on the molecular size. Among the studied azathiones cyclohexyl azathione gave 90% inhibition efficiency at 500 ppm in 1N HCl [12].

Burns and Kumar (1996) employed the tantalum and its alloy to with stand high temperatures and concentrations of organic chemicals including nitric, sulphuric and hydrochloric acid. Tantalum use as liners

or cladding can be cost effective when taken into account the continuous long life, lack of down time, non-fouling characteristics and no side reaction and contamination [13].

Banker (1996) recommended manufacture of purified terepthalic acid (PTA) requires equipment with a combination of superior corrosion resistance & high pressure capability Titanium explosion clad is preferred material for construction of reactors and Heat exchangers [14].

Twomey (1997) developed X-Ray Technique for detecting the Corrosion under insulation (CUI) of piping system without disturbing the insulation; this technique is permitted in many refineries & Petrochemical facilities although technique has some limitations [15].

Kane and Cayard (1998) discussed corrosion-monitoring technique to minimize downtime and equipment failure and to ensure safe and efficient plant operation [16].

Kane et.al (1998) carried out a survey relating to high temperature crude oil corrosion affecting distillation equipment, they recommended that chemical analysis & laboratory testing increases the accuracy of the crude corrosivity assessment but there is still need to be correlated to plant experience [17].

Agarwal (1999) discussed some of the major developments in nickel alloys along with specific commercial applications in petroleum refineries, petrochemical plants and in many other chemical process industries. He claimed that these alloys work well when temperature and acid concentration run high, even in the presence of chloride and other reactive species [18].

Tillack (1999) have discussed a wide range of cast and wrought alloys as material of construction for pressure vessels, piping, fitting, valves and other equipment in petroleum refineries and petrochemical plants. They claimed that these materials with stand temperature to over 650°C (1200°F) and various types of corrosion including oxidation and carburization [19].

Ram Prasad (2000) discussed main corrodents in various refining units, crude oil contain chlorides, organic acid, water & sulphur compounds,

when crude oil is processed at high temperature in atmospheric distillation chlorides present is hydrolyses into HCl which corrode the column and its corrosivity is enhanced in presence of water &H_2S, other corrodent which effect many refining units is Napthenic acid which is corrosive at 225-250^{0}C [20].

Shastri illustrated the use of Organic inhibitors for controlling corrosion in refinery operations which adsorb on the metal through electron rich functional groups, the most common inhibitors used in refining operations are amines, diamines, imidazolines, pyridines & their compounds with fatty acids and sulphonates [21].

Alley and Coble (2003) illustrate the use of two types of organic inhibitors used in controlling corrosion in crude oil distillation unit overhead system, the two type of inhibitors used are Neutralizing inhibitors & Filming inhibitors, Neutralizing inhibitors are those inhibitors which inhibit corrosion by neutralizing HCl as it form at the water dew point in the overhead system and film forming inhibitors are those inhibitors which inhibit corrosion by forming a barrier between metal and the corrosive element in the environment [22].

L.J Rokehar (2003) illustrate that corrosion effect many refinery units and main corrodent are hydrochloric acid, napthenic acid, hydrogen sulfide & hydrogen and also recommend there control by use of filming amines and neutralizing amines [23].

Nitin raut & jignesh patel (2003) illustrate in detail corrosion in stripper overhead airfin cooler of naptha- hydrodesulphurization plant, pretreater unit to catalytic reforming unit at BPCL refinery and also give remedies to control corrosion of such equipment by injection of neutralizing inhibitor in overheads and by provision of water wash facility in stripper [24].

Jaya Rawat, Tushar S. Thorat & N.V.Choudary (2004) discussed Ammonium bisulphide (ABS) corrosion in the overhead circuits of Refinery Amine Regeneration Units (ARU) of Dieselhydrodesulphurization (DHDS) plant.In the overhead system of Amine regeneration unit, high amount of H_2S and NH_3 are present. In condensers/coolers having low

temp-erature zones these gases have the tendency to combine and form Ammonium bisulphide (ABS). ABS crystallizes at temperatures above the dew point of water, its adherence on metal surface causes tube fouling and under deposit corrosion leading to leakages in pipe-lines, tubes of coolers and condensers/exchangers. ABS corrosion is characterized by severe corrosion of carbon steel at high velocity and point of turbulence such as inlet end of tubes and the U bends.

The mitigation of this problem involves estimation of ABS and remedial actions such as use of inhibitor along with controlling process parameters [25].

Survey of the literature reveals that there is relatively a few report on the use of organic inhibitors containing heteroatoms.

Aim of the present investigation

1. To study the corrosion action of three organic inhibitors namely :-
   (a) Decanohydrazide (DH)
   (b) Dodecnohydrazide (DDH)
   (c) Hexadecanohydrazide (HDH)
   (d) Octadecanohydrazide (ODH)
2. To study the inhibition action at different immersion time and temperature.
3. To study the influence of molecular structure on inhibitor performance.

CORROSION

Corrosion can be defined in many ways. The one more preferred in literature is the degradation of useful properties of material as a result of chemical or electrochemical reaction with its environment [26]. Degradation due to purely mechanical forces is not called corrosion but is known as wear, fretting etc. Corrosion can also be defined as conversion of metal back into oxide/sulphites. In some cases chemical or electrochemical attack may be accompanied by physical deterioration and is described by terms corrosion-erosion, corrosion-wear or fretting corrosion.

Trends in corrosion research had changed rapidly over the years. In fifties, polarization studies and their applications had been the topic of interest [27, 28]. In the seventies corrosion research was concentrated on the mechanistic studies on metal dissolution, localized corrosion and high temperature corrosion [29-32]. In recent years corrosion research has been diversified into several newer fields. Optical techniques have revolutionized the field. Surface analytical techniques play a major role since; they give more insight into the understanding of the nature and the influence of surface of surface oxides on the corrosion of metals and alloy. These techniques are helpful to characterize the thickness, the structure and the composition of films. Computers [33] and microprocessors [34] find application in analyzing the corrosion data.

The ultimate objective of all electrochemists, metallurgists and chemical engineers is to understand the mechanism of corrosion and minimize corrosion failures.

2.1 ECONOMIC IMPORTANCE OF CORROSION

Corrosion poses a very serious problem to industries affecting both to the cost and the productivity. Loses due to corrosion are so high that it has assumed great economic importance throughout the world. It is expected that 25% of the total product of the metal and alloys go waste

Chapter -2

Theoretical Background

due to corrosion. The losses due to corrosion, which were modest when process and material were simple, grew exponentially, to the astronomic figures of over Rs. 6,40,000 million per year by 1977, amounting for losses equal to about one percent of the gross world product [35].

Even in the industrially developed countries like USA and UK, corrosion is posing very serious problems, which can be appreciated by the fact that Canada is spending $1 billion annually to control corrosion, while in UK the total loss due to corrosion is of the order of £600 million [36]. According to NACE (International) bulletin [37] the annual losses due to corrosion in USA were estimated to be more than $300 billion. In India the annual losses due to corrosion has increased to more than Rs.25,000 crores per year.

Thus from economic point of view, it is necessary for corrosion specialists to study corrosion mechanism and various ways and means to minimize corrosion damage.

2.2 CLASSIFICATION OF CORROSION

Corrosion has been classified in many different ways as low temperature and high temperature corrosion, direct oxidation and electrochemical corrosion, etc. The preferred classification is (i) Wet or electrochemical corrosion (ii) Dry or chemical corrosion.

(i) Wet or Electrochemical Corrosion, which involves an interface. It can be further separated into:

- Separable anode / cathode type: In these cases certain areas of the metal can be experimentally identified as predominantly anodic or cathodic. The distances of separation of these areas may be very small, of the order of fractions of millimeter. There is a macroscopic flow of charge through the metal.
- Interfacial anode / cathode type: In this type one entire interface is cathode and the other is the anode and the charge is transported through a file of reaction product on the metal surface.

- Inseparable anode / cathode type: Here the anodes and the cathodes cannot be distinguished by experimental methods, though there presence is postulated by theory, e.g. the uniform dissolution of the metal in fused salt non-aqueous solutions, acid, alkaline or neutral solutions.

(ii) Dry or Chemical Corrosion which involves direct chemical reaction of a metal with its environment. There is no transport of electric charge and the metal remains film free. This would include corrosion in gaseous environments when the reaction product is volatile, corrosion in liquid metals, fused halides and organic liquids. A general scheme for the classification of corrosion processes is presented separately in the form of a Table 1.1. Various important form of corrosion with definitions and examples are summarized in Table1.2

2.3 ELECTROCHEMICAL THEORY OF CORROSION

Most of the corrosion reactions, especially those occurring in aqueous media are electrochemical processes. The overall corrosion process is the contribution of two reactions, the oxidation of metal (anodic process) and an equivalent reduction reaction (cathodic process). An oxidation reaction is indicated by production of electrons as given below:

$$M \rightleftharpoons M^{+} + e^{-} \qquad \text{--------(1)}$$

This reaction constitutes the basis of corrosion of metals. In a similar fashion, a reduction reaction is indicated by the consumption of electrons. For every oxidation reaction there must be a corresponding reduction reaction. In aqueous solutions, various reduction reactions are possible depending upon the system. Some examples of reduction reactions are:

Hydrogen evolution

$2H^{+} + 2e^{-} \rightarrow H2$ (in acidic system) --------(2)

Oxygen reduction

$O_2 + 4H^{+} + 4e^{-} \rightarrow 2\ H_2O$ (in acidic solution) --------(3)

$O_2 + 2H_2O + 4\ e^{-} \rightarrow 4\ OH^{-}$ (in neutral and alkaline solution -----(4)

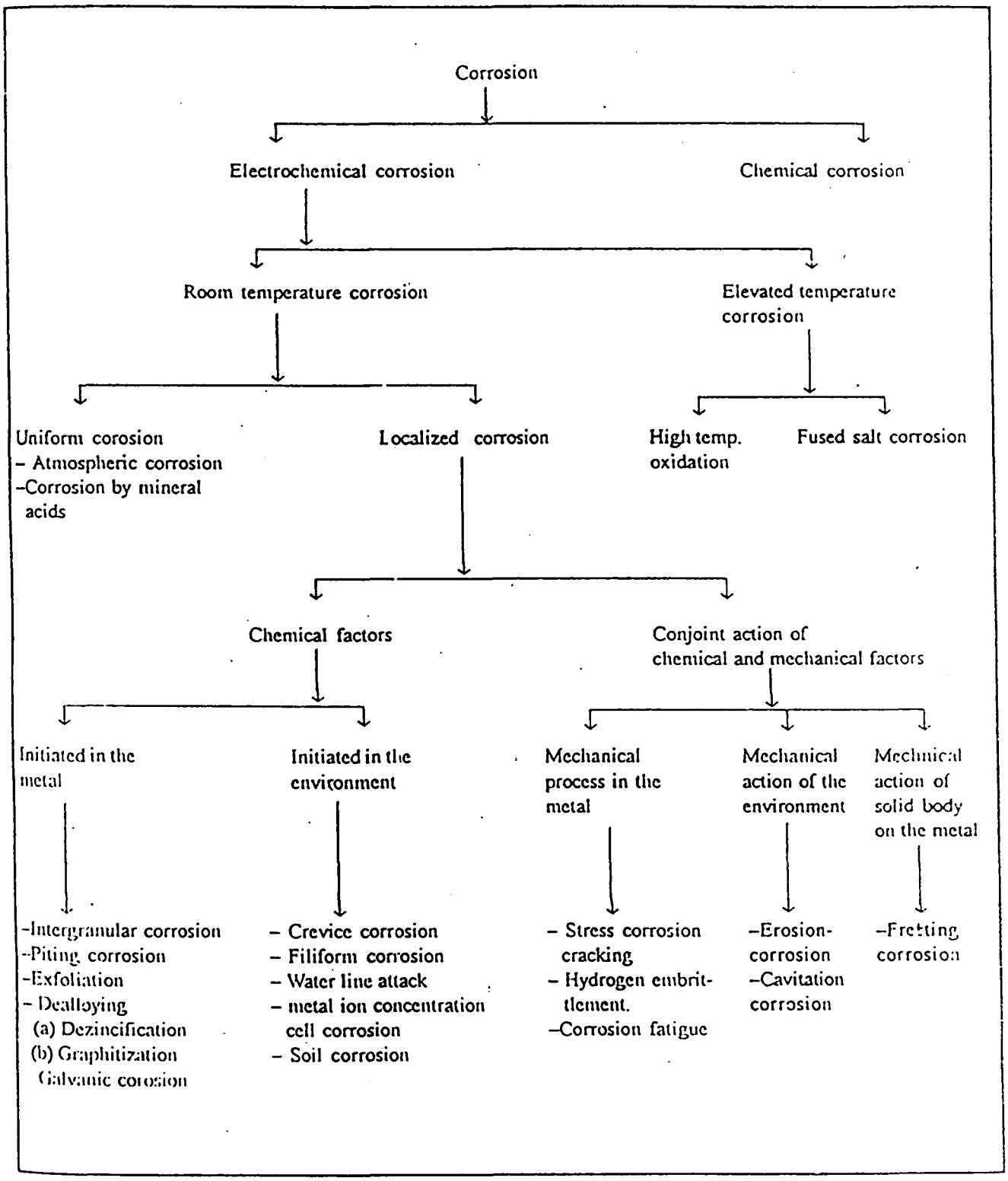


Table 1.1 Classification of corrosion processes

Table 1.2 Various important forms of corrosion with examples

S. No.	Corrosion type	Definition	Examples
1.	Dry corrosion	Involving chemical reaction with non-electrolytic gas or liquid.	Corrosion of steel with SO_2, CO_2, O_2, etc.
2.	Wet corrosion	Corrosion in contacts with electrolyte such as aqueous solution of salt, alkali and acid.	Corrosion of steel in sea water, acids and alkalis.
3.	Uniform corrosion	Uniform attack of electrochemical or chemical reaction over the entire surface.	Steel immersed in dilute sulphuric acid.
4.	Pitting corrosion	Localized attack in the form of pit.	Stainless steel, aluminium alloys, copper alloys, and nickel alloys immersed in chloride solution.
5.	Crevice corrosion	Intense localized corrosion in shallow holes.	The crevices under bold and rivet heads.
6.	Galvanic corrosion	Dissimilar metals immersed in a corrosive media and connected electrically	Zinc and iron in salt solution.
7.	Intergranular corrosion	corrosion occurring in the vicinity of grain boundaries.	Weldments of stainless steel
8	Stress corrosion cracking	Cracking caused by simultaneous presence of tension stress and particular corrosion medium.	Season cracking of brass and caustic embrittlement of steel.
9	High temperature oxidation	Oxidation reaction with the products of fuel combustion.	Corrosion of steel with combustion products such as Co_2, SO_2, O_2, etc.
10.	Erosion corrosion	Acceleration of corrosion because of relative movement between corrosive fluid and the metal.	Corrosion in pumping equipment, corrosion in the area between bearings and shafts.
11.	Corrosion fatigue	Combined action of corrosive medium and variable stresses.	Heat exchanger tubes of chemical equipments.

Metal ion reduction

$M^{+n} + e^- \rightarrow M^{+(n-1)}$ --------(5)

Metal deposition:

$M^{+n} + ne^- \rightarrow M$ --------(6)

Oxidation reactions are known as anodic reactions while reduction reactions as cathodic. During the corrosion more than one anodic and cathodic reaction may occur. Oxidation-reduction (redox) reactions can be understood by the example of corrosion of mild steel in sulphiric acid contaminated by ferric ions. Anodic reaction will occur as follows:

$M \rightleftharpoons Mn^+ + ne^-$ -------(6a)

All the components elements of mild steel (e.g. Fe, Mn, etc.) go into the solution as their respective ions. The electrons produced by these anodic (oxidation) reactions will be consumed by the cathodic (reduction) reactions. In this case, reaction (5) can be represented as follows:

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ --------(7)

Removing one of the available cathodic reactions e.g. reaction (7) by removal of the Fe^{3+} ions will reduce the corrosion rate.

When a metal or alloy is immersed in a corrosive environment (conductive) different potential zones are developed on the surface of metal of alloy due to the presence of different metallic phases, grain boundaries, segregates, crystalline imperfections, impurities, etc. This difference in potential leads to the formation of anodic and cathodic areas on the metallic surface where oxidation and reduction reactions occur, respectively. These areas result in the formation of local action cells on the metallic surface. Local action cell can also be formed where there are variations in the environment or in temperature. The electrode potential is calculated from the Nernst equation:

$$E = E_0 + \frac{RT}{zF} In \frac{(ox)}{(red)} \qquad \text{--------(8)}$$

Where,

Eo = Standard electrode potential

R = Gas, constant (1.98 cal/gm. Equivalent)

F = Faraday constant (96,500 coulombs/gm equivalent)

T = Absolute temperature

Z = Number of the electrons transferred in the reaction

(ox) = Concentration of oxidised species (mol/1)

(red) = Concentration of reduced species (mol/1)

2.4 Thermodynamics Principles of corrosion

In most of the cases, metallic state represents the state of high energy. Therefore, metal have a natural tendency to react with other substances and go back to lower energy state with subsequent release of energy. All Metals show decrease in free energy by undergoing reaction with the environment, (except noble metals, which are found in native state in nature); Thermodynamic stability of chemical compounds is determined by the signs and the change in the free energy (ΔG), when they are formed from simple substances.

Free energy is the thermodynamics property that expresses the resultant enthalpy of substance and its inherent probability. At constant temperature free energy can be expressed as follows:

$$\Delta G = \Delta H - T\,\Delta S \qquad \text{----------(9)}$$

When the reaction are at equilibrium then:

$$\Delta G^0 = -RT \ln Keq \qquad \text{----------(10)}$$

Where ΔG is the change the free energy, ΔH is the change in enthalpy, ΔS is change in entropy and T is absolute temperature.

When ΔG^0 is standard free energy, R is gas constant and Keq is equilibrium constant. The potential of a reaction is related to its free energy (ΔG) by:

$$\Delta G = -z\,FE \qquad \text{----------(11)}$$

A negative value for the free energy corresponds to a spontaneous reaction, whereas a positive value of ΔG indicates that the reaction has no tendency to proceed. The change in free energy accompanying an electrochemical or corrosion reaction can be calculated from knowledge of the cell potential of the reaction. It is the redox potential by which one can predict whether a metal will corrode in a given environment or not.

2.5 METHODS OF CORROSION CONTROL

The methods of corrosion control are many and varied. Details of these various methods may be found in the extensive literature on corrosion control [38-40].

2.6 PREVENTION OF CORROSION BY APPLICATION OF INHIBITORS

2.6.1 Definition of Inhibitors

The definition of an inhibitor favored by the NACE is "a substance which retards corrosion when added to an environment in small concentrations" [41] and the recent ISO definition of an inhibitor is "chemical substance which decreases the corrosion rate when present in the corrosion system at a suitable concentration without significantly changing the concentration of any other corrosive agent" [42]. Inhibitors may also be defined on electrochemical basis as substances that reduce the rates of either or both of partial anodic oxidation /cathodic reduction reaction.

From 19th century onwards-vegetable wastes, plant extracts [43, 44] were used as inhibitors. Putilova et al [45] have reviewed metallic corrosion inhibitors. Review on organic inhibitors [46-48] and organic sulphur compounds [49] have been published. Several books have been published on this subject [50,51]. Besides, the University of Ferrara, Italy, conducts a symposium on corrosion inhibition once in five years [52]. All the international seminars on corrosion discuss the

developments and application of corrosion inhibitors [53,54]. Various books on corrosion, review the subject in a precise manner [55, 56].

2.6.2 Classification of Inhibitors

Inhibitors are classified in different ways. Depending on the environment, they are called acid inhibitors, neutral and alkaline inhibitors and vapour phase inhibitor. Depending on the mechanism of inhibition they are classified as cathodic, anodic and mixed inhibitors.

According to Putilova [45] inhibitors are of three types:

Type A

Those inhibitors, which function by forming a protective layer on the surface of metal, come under this type. Inhibitors of this type are commonly used and represent the largest class of inhibiting substances.

Type B

This type of inhibitors reduces the aggressiveness of medium towards the metal and may be called deactivators of the medium. These include sulphites (Na_2SO_3), which retard corrosion on water by combining with dissolved oxygen.

Type AB

Hydroxides or carbonates of the alkali metals (NaOH or Na_2CO_3) are added to water to prevent the corrosion of steel articles by lowering the hydrogen ion (H^+) concentration. A very thin film of insoluble iron hydroxide or carbonate is also formed on metal surface.

2.6.2.1 ACID INHIBITORS

This may be further classified into inorganic and organic inhibitors.

(i) Inorganic inhibitors

In strong acid solutions, Br^-, I^- have found to be effective inhibitors [57]. The oxides like As_2O_3, Sb_2O_3 have been reported as inhibitors in acid media. These substances get deposited [58] in the form of metal on iron and increase the hydrogen over-voltage and subsequently reduce the

corrosion. Recently addition of heavy metal ions like Pb^{2+}, Mn^{2+}, Cd^{2+} is found to inhibit corrosion or iron in acids. This effect is explained as due to under potential deposition of metal ions leading to complete coverage on the iron surface [59].

(ii) Organic Inhibitors

These are organic substances containing N, S, or O as reactive centre though which they get adsorbed on the metal surface and inhibit corrosion of metals in acid environment. The prominent examples of acid inhibitors are acetylinic alcohols, aldehydes, mercaptans, hetroyclic compounds and thiourea derivatives [60,61].

An organic corrosion inhibitor can be anodic, cathodic or both depending on its reaction at the metal surface and how the potential of the metal is affected [62]. Generally cathodic inhibitors increase cathodic polarization and shift the corrosion potential to more potential to more negative values, and anodic inhibitors enhances anodic polarization and shift the corrosion potential to more positive values.

The effectiveness of an organic inhibitor depends mainly on (i) Size (ii) Carbon chain length (iii) Bonding strength to metal surface. (iv) Aromaticity and or conjugated bonding (v) Nature and number of bonding atoms.

2.6.2.2 NEUTRAL / ALKALINE INHIBITORS

These inhibitors include cathodic inhibitors (which increase cathodic polarization), anodic inhibitors (which enhance the anodic polarization) and mixed or general inhibitors (which act on both cathodic and anodic areas).

Anodic inhibitors forms are oxide or some other insoluble film. Insufficient concentration of anodic inhibitors will lead to severe pitting.

Sodium chromate is one of the most widely used and efficient inhibitors. Sodium silicate is generally used in hot water systems. The other compounds used in neutral and alkaline media are borates, molybdates and salts of organic acids like benzoates and salicylates.

2.6.2.3 VAPOUR PHASES INHIBITORS (VPI)

Those substances whose vapour pressure is sufficiently high act as vapour phase inhibitors. The vapour pressure of these compounds at room temperature is usually between 0.1 and 1.0 mm mercury, so that the inhibitors sufficiently fast to ensure its adequate availability in the vicinity of the metal surface.

The prominent examples of vapour phase inhibitors are dicyclohexyl ammonium nitrite benzothiazole for protecting copper, phenylthiourea and cyclohexylamine chromate for brass. Dicyclohexylamine nitrite is said to protect both ferrous and non-ferrous parts.

The inhibitor vapour condenses on contacting a metal surface and is hydrolyzed by moisture present to liberate nitrite and benzoate ions, which in presence of available oxygen are capable of passivating steel as they do in aqueous solution.

2.6.2.4 ANODIC INHIBITORS

The substances, which retard the anodic area by acting on the anodic sites and polarize the anodic reaction, are called anodic inhibitors. In the presence of anodic inhibitors, displacements in corrosion potential (Ecorr) takes place in positive direction and suppress corrosion current (I_{corr}) and reduces corrosion rate. The curve E^{a}_{corr} represents the anodic reaction while E^{a}_{corr} represent the cathodic reaction and the point B where both anodic and cathodic reaction intersect corresponds to corrosion potential (E_{corr}) and corrosion current (I_{corr}). The substances, which retard the anodic reaction to enhancement of anodic polarization. In this situation, anodic curves become E^{a}_{corr} (Figure 1.2a) and the current E^{a}_{corr} corresponding to 0 is less than I_{corr} (corrosion current in the absence of the inhibitors) and the rate of corrosion is decreased. Anodic inhibitors which causes a large shift in the corrosion potential are called passivating inhibitors, if used in insufficient concentration, they cause pitting and sometimes an increase in corrosion rate.

Anodic inhibitors are of two types.

i) Oxidising anodic inhibitors – They inhibit corrosion by passivating the metal surface eg. Chromate, nitrite [63].

ii) Non-oxidising anodic inhibitors – They inorganic anions such as molybdate benzoate, phosphate are the examples of non-oxidising type anodic inhibitors.

These inhibitors slow down anodic reaction by forming passive film on the metal surface in presence of oxygen.

2.6.2.5 CATHODIC INHIBITORS

Those substances, which reduce the cathodic area by acting on the cathodic sites and polarize the cathodic reactions, are called cathodic inhibitors. They displace the corrosion potential (E^c_{corr}) in the negative direction and reduce corrosion current, thereby retard cathodic reaction and suppress the corrosion rate (Figure 1.2b). In this situation, the point of intersection is at 0 and corresponding corrosion current (I^c_{corr}) will be lower than that without inhibitor (I_{corr}). The cathodic inhibitors, with a few exceptions [64] do not read to intensified or localized attack, since, cathode areas are not attacked during corrosion.

Cathodic inhibitors can be divided into three categories.

i) Cathodic poisons – The substances which interfere with the formation of hydrogen atoms or recombination of hydrogen atoms to H_2 gas are know as cathodic poisons e.g. arsenic and antimony salts.

ii) Oxygen scavangers – The substance which inhibit the corrosion by removing dissolved oxygen are called oxygen scavangers e.g. hydrazine and sodium sulphite.

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \quad \text{----------(23)}$$

$$N_2H_4 + O_2 \rightarrow N2 + 2H_2O \quad \text{----------(24)}$$

The advantage of hydrazine over sulphite is that it does not increase hardness of water, which in turn prevents scale formation in boiler.

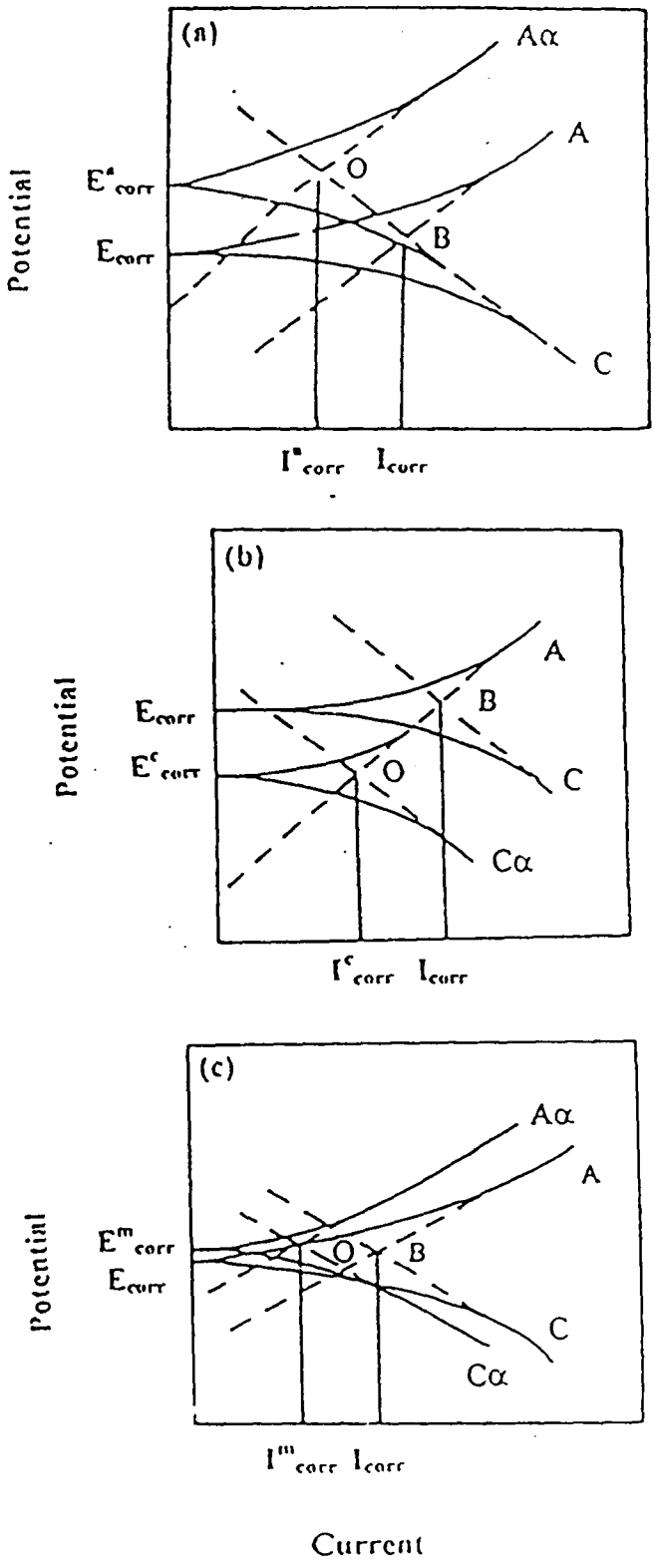


Figure 1.2 Mechanism of action of corrosion inhibitors based on polarisation effects

iii) Cathodic precipitate (Filming inhibitor)-Calcium bicarbonate and zinc sulphate are the example of filming type inhibitors. The cation parts of these inhibitors migrate towards cathode and react with cathodically formed alkali to produce insoluble protective film on cathode and thereby inhibit cathodic reaction.

$$Ca^{++} + 2HCO_3 + OH^- \rightarrow \quad CaCO_3 + HCO_3^- + H_2O \quad ---(25)$$

$$Zn^{++} + OH \rightarrow \quad Zn(OH)_2 \quad ----(26)$$

2.6.2.6 MIXED INHIBITORS

There are a number of inhibitors, which inhibit corrosion by interfering with both the anodic and cathodic reactions and are called mixed inhibitors. This type of inhibition can be represented by Figure 1.2c. The anodic and cathodic reaction are represented by $E^m_{corr}A$ and $E^m_{corr}C$ respectively and corrosion current I^m_{corr} in presence of such type of inhibitors in considerably less than that in their absence. Gelatin, Glue and other high molecular weight substances fall in this category. Machu [65,66] claims that there is mainly due to formation of porous layer, which increases the electrical resistance of the surface layer.

2.7 MECHANISM OF INHIBITION IN ACIDS

The inhibitive action of organic compounds occurs on the metallic surface due to interaction between the inhibitors and the metal surface by adsorption phenomenon. In this process [46] the molecules are held on the surface of the adsorbent by valence forces i.e., variation in the charge from one phase to the other. Therefore, the molecular structure of the inhibitors assumes special significance [67]. The electron density at atoms of functional group constituting a reaction centre affects the strength of the adsorption bond [68].

2.7.1 FACTORS AFFECTING ADSORPTION MECHANUSM

(i) Surface charge in Metal

The magnitude and sign of the surface charge of the metal play a very important role for the establishment of the adsorption bond. The effects exercised by organic inhibitor on the electrode reactions must be connected with the modification induced in the structure of the electrochemical double layer because of their adsorption. In solution the charge on a metal can be expressed by its potential with respect to the zero charge potential. This potential, often referred to as the ϕ potential, is more important then the potential on a hydrogen scale and sign of these potentials are different [69]. As the potential becomes more positive, the adsorption of anions is favored and as the potential becomes more negative, the adsorption of cations is favored.

(ii) Reaction of Adsorbed Inhibitors

In some cases, the adsorbed corrosion inhibitors may react to form a product by electrochemical reduction, which may also be inhibitive in nature. Inhibition due to the added substances has been termed as primary inhibition and that due to the reaction product, secondary inhibition [70]. In such cases, the inhibition efficiency may increase or decrease with time according to whether the secondary inhibition is more or less effective than the primary inhibition [71].

(iii) Interaction of Absorbed Inhibitor Species

Lateral interactions between adsorbed inhibitor species become significant with increase of surface coverage of the adsorbed species. This lateral interaction may be either attractive or repulsive. Attractive interaction occurs between molecules containing large hydrocarbon components. Repulsive interactions occur between ions or molecules containing dipoles and lead to weaker adsorption at high coverage [72].

(iv) Interaction of the Inhibitors with Water Molecules

The surface of metal is aqueous solution are covered with adsorbed water molecules. Adsorption of inhibitors takes place by the displacement of adsorbed water molecules from the surface, which

involves free energy for adsorption. It is found to increase with the energy of solvation of the adsorbing species [73].

(v) Structure of Inhibitors and their Adsorption

Inhibitors can bond to metal surface by electron transfer to the metal to form adsorption bond. Generally the inhibitors are the electron donors and the metal is the electron acceptor. The strength of this bond depends on the characteristic of both the adsorbate and adsorbent. Electron transfer from the adsorbed species is favored by the presence of relatively loosely bound electrons, as may be found in anions and neutral organic molecules containing lone pair electrons of π-electron systems associated with multiple, especially triple bonds or aromatic rings.

Most organic compounds have at least one polar atom i.e. nitrogen, sulphur, oxygen and in some cases selenium and phosphorous. In general, the polar atom is regarded as the reaction centre for the establishment of the chemisorption process [74]. In such cases, the adsorption bond strength is determined by the electron density of the atom acting as the reaction center and by the polarizability of the polar atoms. The effectiveness of the polar atoms with respect to the adsorption process varies in the following sequences [75].

Selenium > Sulphur > Nitrogen > Oxygen

The importance of electron density in chemisorption of organic substances in relation to inhibition phenomena has been evaluated. The idea of electron density acquires particular importance in aromatic or heterocyclic inhibitors whose structure may be affected by the introduction of substituents in different positions of the rings [69]. The availability of electron pairs for the formation of chemisorption bonds can thus be altered by regular and systematic variations of the molecular structure.

2.7.2 INFLUENCE OF INHIBITORS ON CORROSION REACTION

An inhibitor may decrease the rate of anodic process, the cathodic process or both processes. The change in corrosion potential on addition of the inhibitor is the indication of a retarded process [60]. Shift of the corrosion potential in the positive direction indicates mainly retardation of the anodic process (anodic control) whereas shift in the negative direction indicates retardation of the cathodic process (cathodic control). Little change in the corrosion potential suggests that both anodic and cathodic processes are retarded.

In the presence of an inhibitor, a shift of polarization curves without a change in the Tafel slope indicates that the adsorbed inhibitor acts by blocking active sites so that reaction cannot occur rather than affecting the mechanism of the reaction [76]. A change in the Tafel slope is the indication of affecting the mechanism of the reaction.

Inhibitor in acid solution affects the corrosion reactions of metals in the following ways:

(i) Formation of a Diffusion Barrier

The adsorbed inhibitor, which forms a surface film on the metal surface, can act as a physical barrier to restrict the diffusion of ions or molecules to or from the metal surface and thus retard the corrosion reaction. This type of behavior occurs in inhibitor containing large molecules [77].

(ii) Blocking of Reaction Sites

The inhibitors may adsorb on the metal surface to prevent the surface metal atoms from participating in either the anodic or cathodic reaction of corrosion. This blocking process reduces the surface metal at which these reaction can occur, and hence the rates of these reactions. The mechanisms of the reactions are not affected and the Tafel slopes of the polarization curves remain unchanged. Adsorption of inhibitors at low surface coverage tends to occur at anodic sites, causing retardation of the anodic reaction. At high surface coverage, adsorption occurs on both anodic and cathodic sites, and both reactions are inhibited.

(iii) Participation in the Electrode Reactions

The electrode reactions involve the formation of adsorbed intermediate species with surface metal atoms. The presence of adsorbed inhibitors will interfere with the adsorbed intermediate but the electrode processes may then proceed by alternative paths through intermediates containing the inhibitor. In these processes, the inhibitor affects the reaction and the inhibitor remains unchanged with a change in the Tafel slope [78]. Inhibitors may retard the rate of hydrogen evolution on metals by affecting the mechanism of the reaction with the increases in Tafel slopes of cathodic polarization curve. This effect has been observed on iron in the presence of inhibitors such as phenylthioureas [79].

(iv) Alternation of the Electrical Double Layer

The adsorption of ions or species, which can form ions on metal surface, will change the electrical double layer at the metal solution interface, and this in turn will affect the rates of the electrochemical reactions.

(v) Adsorption Isotherms

An adsorption isotherm gives the relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the concentration of the species in solution [80]. Various adsorption isotherms have been formulation. Table 1.4 gives the list of isotherms and their corresponding equations [81].

Interpretation of the inhibition characteristics of organic molecules can be made by fitting the data to one of the adsorption isotherms.

2.8 TECHNIQUES FOR CORROSION INHIBITION MONITORING

The various techniques employed for corrosion monitoring have been classified as:

(i) Non-Electrochemical Methods.

(ii) Electrochemical Methods

(i) Non-Electrochemical Methods

These include techniques like weight-loss measurement and gasometric methods. The main disadvantage of these methods is that these require relatively long exposure times of the corroding systems. Also the non-electrochemical methods are in general restricted to systems, which do not form adherent layer of corrosion products.

(a) Weight Loss Measurements

This method is the most reliable method. The electrochemical measurement results are usually compared with weight loss data. Here the change in weight of the specimen is determined by immersing the specimen in the corrosive medium for a fixed time. The rate of metal removal due to corrosion is calculated from:

$$R = KW/ATD$$

Where R is the corrosion rate, K is a constant; W is the weight loss to the nearest 0.0001g. A is the area of the specimen to the nearest 0.01 sq. cm., T is the time exposure to the nearest 0.01 hour and D is the density in g/cu.

A variety of units have been used in the literature to express the corrosion rate. Using the units for T, A, W and D in the above equation corrosion rate can be calculated in different units with the appropriate value of K (Table 1.5). If desired, these constants may also be used to convert corrosion rates from one set of units to another. To convent corrosion expressed in unit x to a rate in unit y, multiply by K_y/K_x. e.g., if R is 10 mpy the rate in mm/yr would be:

$$10\ (8.76 \times 10^4/3.45 \times 10^6) = 0.254\ \text{mm/yr.}$$

(b) Gasometric Methods

This method yields reliable and accurate with a high degree of reproductively. In this method the volume of hydrogen gas (in acid corrosion) involved during a corrosion reaction is directly measured at a constant temperature. The corresponding metal loss can be calculated. This technique has been used for the inhibitors studies by Nathan [82]. Mathur et al [83] have designed a gasometric unit with

which corrosion rates could be monitored under controlled conditions of temperature the pressure without any aqueous correction. Singh et al [84] have designed apparatus for measuring adsorbed hydrogen gas and hydrogen diffusion. Also this technique has been successfully applied for the determination of corrosion kinetic parameters by them. However this technique has certain limitation such as it can be applied to a strong oxidizing medium like nitric acid, to systems where the inhibitor used undergoes reduction with the hydrogen gas evolution, etc.

(ii) Electrochemical Methods

The electrochemical methods are most widely used for the study of inhibitors. Electrochemical methods are finding increased use in corrosion research and in engineering applications. Such methods are practical because the corrosion behavior of material-electrolyte combinations is a direct function of the mechanism as well as kinetics of the electrochemical methods can be used, in field or in laboratory, to measure corrosion rates without removing the specimen from the environment or altering the sample itself.

(a) Polarization Methods

The electrochemical polarization of metallic sample is accomplished with a power supply known as potentiostat. An auxiliary electrode supplies the current to the working electrode (test specimen) in order to polarize it. The potential between the working electrode and reference electrode is monitored or set at a fixed value. Figure 1.3 illustrates schematically a typical experimental arrangement.

The system is designed so that only an extremely small current can pass between the reference electrode and the working electrode. The current needed to polarize the working electrode is supplied from the auxiliary electrode. Several American Society for Testing and Materials (ASTM) standards discuss methods for performing these experiments [85, 86].

In this method the behavior of inhibitor is understood by drawing a Tafel plot (Figure 1.4) in absence and presence of inhibitor. The percentage inhibition is calculated from the formula.

$$IE\% = \frac{I^{\circ}_{corr} - I_{corr}}{I^{\circ}_{corr}} \times 100 \qquad ----(27)$$

I° = Corrosion current density (corrosion rate) in absence of inhibitor,

I = Corrosion current density (corrosion rate) in presence of inhibitor.

The corrosion rate is determined from the polarization data in two ways:

1. Tafel extrapolation method
2. Linear polarization method.

In Tafel extrapolation method the linear portion of the Tafel curve is extrapolated. The point of intersection is referred to as I_{corr}.

Linear polarization method provides the value of absolute corrosion rate from the following relation.

$$I_{corr} = \frac{\beta_a \times \beta_c}{2.3 (\beta_a + \beta_c)} \times \frac{1}{R_P} \qquad --- (28)$$

Where β_a and β_c are Tafel constants, $1/R_P = \Delta I / \Delta E$ = polarization conductance.

2.9.1 INHIBITION OF CORROSION OF IRON AND STEEL IN ACIDS

Inhibitors play an important role in controlling the corrosion of metal in acid solutions. Inhibitors are used to minimize the corrosive attack of metallic materials. Inhibitors can protect metallic materials, especially ferrous metals and alloy in mineral acids and various organic acids.

The main features of effective inhibitors are as follows:

(i) Should effectively inhibit the metal dissolution.

(ii) Should be effective at low concentrations.

(iii) Should be thermally stable and chemically inert.

(iv) Should inhibit hydrogen uptake by the metal.

(v) Should possess good surfactant and good foaming characteristics.

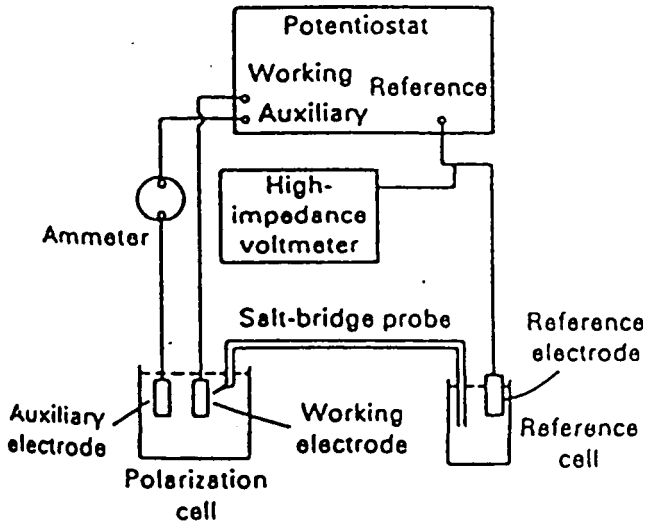


Figure 1.3 Instrumental setup for electrochemical polarisation experiments.

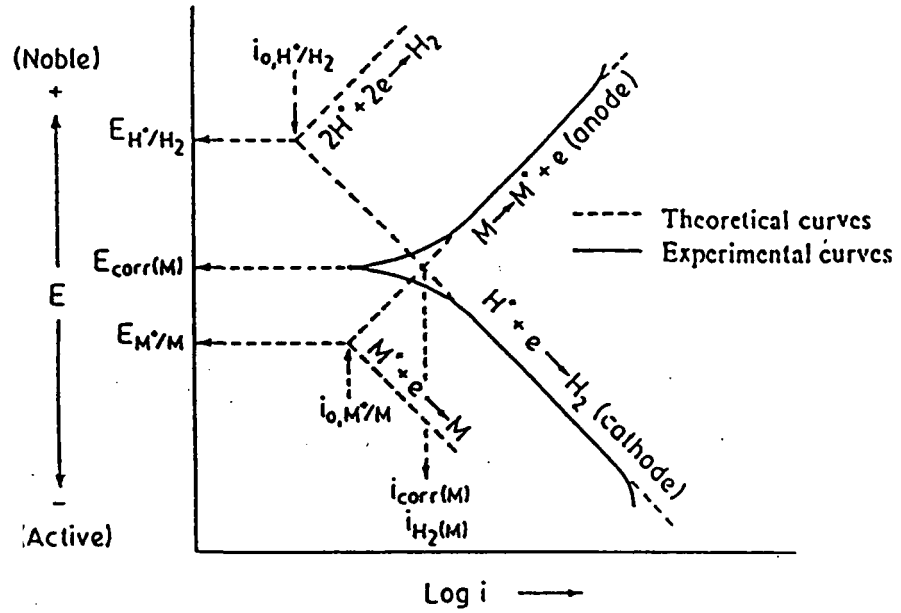


Figure 1.4 Polarisation curves for a corroding electrode.

E_{corr} = Corrosion potential
i_{corr} = Corrosion current

Chapter-3

Experimental

3.0 MATERIALS

3.1 TEST SPECIMEN

3.1.1 WEIGHT LOSS STUDY

Cold rolled mild steel strips of size 2 cm x 2.5 cm x 0.05 cm and composition as given below were used for 20% acidic solutions for weight loss study.

C	Mn	Si	P	Fe
0.14%	0.35%	0.17%	0.03%	Remainder

3.1.2 FOR ELECTROCHEMICAL TESTS

Cold rolled mild steel strips having working areas of 1 cm^2 and composition same as above were used for all electrochemical tests.

3.2 TEST SOLUTIONS

The Hydrochloric acid (MERCK) of AR grade was used as corrosive media. The double distilled water was used to prepare all the test solutions. The test solution of inhibitor contains 5% of acetone or ethanol as solvent for solubilizing the organic compounds used as corrosion inhibitors.

3.3 INHIBITORS USED

Four inhibitors were synthesized in the laboratory. They are listed below:

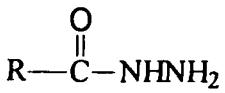


Table-1 Name and molecular formula of inhibitors

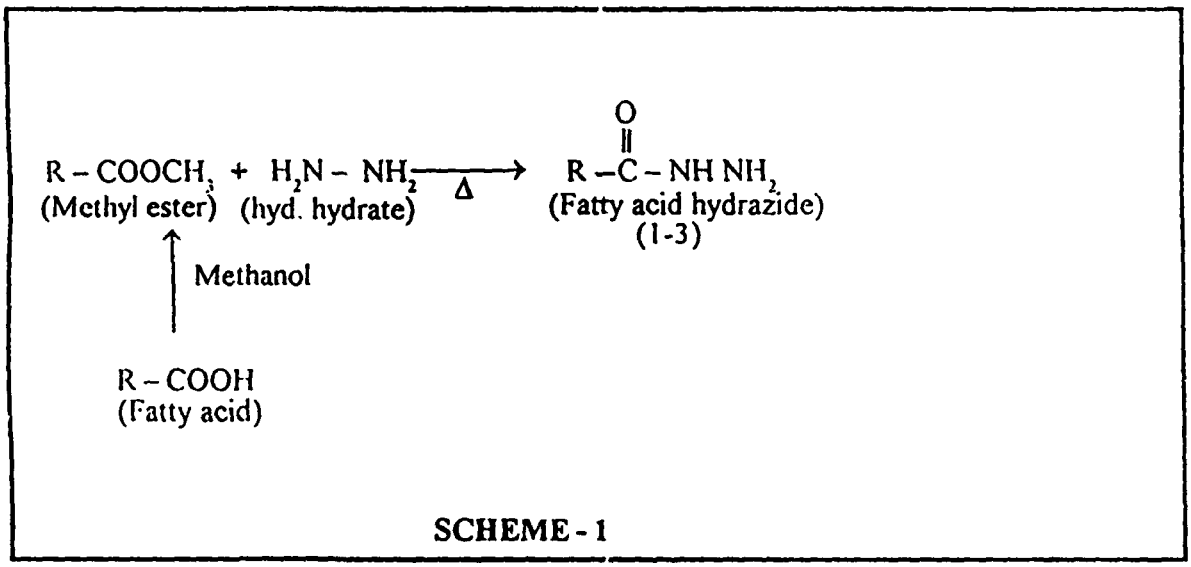
S.N	Inhibitor name	Molecular Structure	M.W
1	Decanohydrazide (DH)	$CH_3\text{-}(CH_2)_8\text{-}C(=O)\text{-}NHNH_2$	186.27
2	Dodecanohydrazide (DDH)	$CH_3\text{-}(CH_2)_{10}\text{-}C(=O)\text{-}NHNH_2$	214.32
3	Hexadecanohydrazide (HDH)	$CH_3\text{-}(CH_2)_{14}\text{-}C(=O)\text{-}NHNH2$	270.43
4	Octadecanohydrazide	$CH_3\text{-}(CH_2)_{16}\text{-}C(=O)\text{-}NHNH_2$	298.48

3.4 SYNTHESIS OF FATTY ACID HYDRAZIDES

The fatty acids were esterified with methanol . A mixture of methyl esters of fatty acids(0.01M), hydrazine hydrate 99-100 %(0.03 M) and ethanol (25 ml) wasrefulxed for 8 hours. The solid that separated on cooling the concentrated reaction, mixture was filtered, washed with little ethanol, then with ether and dried. It was then recrystallized from boiling water.

Characterization data of compounds are given below:-

Compound No.	Name of Compound	Yield (%)	M.P (^{0}C)
1	DDH	95	113-114 ^{0}C
2	DH	91	92-95 ^{0}C
3	HDH	92	78-79 ^{0}C
4	ODH	89	81-82 ^{0}C


R – COOCH3 + H2N – NH2
(Methyl ester) (hyd. hydrate)
Δ
O
R – C – NH NH2
(Fatty acid hydrazide)
(1-3)
Methanol
R – COOH
(Fatty acid)

SCHEME - 1

3.5 DETERMINATION OF THERMODYNAMIC PARAMETERS

3.5.1 Determination of Activation Energy

The values of activation energy (E_a) were calculated using the Arrhenius equation

$$\ln (r_2/r_1) = (-E_a \times \Delta T) / (R \times T_2 \times T_1)$$

Where r_1 and r_2 are corrosion rate at temperature T_1 and T_2 respectively, ΔT is the difference in temperature (T_2-T_1).

3.5.2 Determination of Free Energy of Adsorption

The free energy of adsorption at different temperature was calculated using the equation given below:

$$\Delta G_{ads} = -RT \ln (55.5K)$$

and K is given by:

$$K = \theta/C (1-\theta)$$

where θ is degree of coverage on the metal surface, C is concentration of inhibitor in mole/lit, T is temperature, R is a constant and K is equilibrium constant.

3.6 TECHNIQUES EMPLOYED

The experimental work was carried out with the help of the following techniques:

1. Weight Loss Method
2. Potentiostatic Polarization Technique

3.6.1 WEIGHT LOSS METHOD

Specimens of size2.0 cm x 2.0 cm x 2.5 cm were cut from the mild steel and mechanically polished with 1/0 to 4/0 grades of emery papers. After polishing, the specimen with acetone. The weight of the specimen was measured before exposing it to corrodent on an electrical balance. During weight loss experiments, the specimens were fully immersed in 200 ml test solution using beaker of 250 ml capacity. After a definite exposure time, the specimen was taken out and washed with distilled water. Specimens were then dried and loss in weight was recorded. The thermostatic chamber was used for carrying out the weight loss experiments at higher temperatures. Thermostat was within an accuracy of ± 2°C. The percentage inhibition efficiency and surface coverage (θ) were calculated using the following equation:

$$IE(\%) = \frac{W_o - W}{W_o} \times 100$$

$$\theta = \frac{W_0 - W}{W_0}$$

Where

IE (%) = Percentage Inhibitive Efficiency

θ = Surface Coverage

W_0 = Wt. Loss or Corrosion Rate in Uninhibited System

W = Wt. Loss or Corrosion Rate in Inhibited System

2.6.2 POTENTIODYNAMIC POLARIZATION TECHNIQUE

The following instruments were used for carrying out the polarization studies:

(I) Potentiostat (EG & G PARC model: 173)

(i) Log current converter (model: 376)

(ii) Universal programmer (model: 175)

(iii) X-Y Recorder (model RE 0089).

For potentiodynamic polarization study, working electrodes 1 cm x 1 cm with a tag of 4 cm were cut from the mild steel sheet and polished with 0/0 to 4/0 grade of emery papers. The specimens were then thoroughly washed with distill water and finally with acetone, unwanted area of the electrode was coated with lacquer to get a well defined area. The polarization studies were carried out using Potentiostat (EG 7 G PARC model: 173), Universal programmer (model: 175), X-Y Recorder (model RE 0089).

All the experiments were carried out at (26 ± 2°C). A platinum foil of 3 cm x 3 cm was used as the auxiliary electrode and a saturated calomel electrode was used as reference electrode.

All the potentials were measured against a saturated calomel electrode. The inhibition efficiency was calculated using the following equation:

$$IE\ (\%) = \frac{I_{o\ corr} - I_{corr}}{I_{o\ corr}} \times 100$$

$I_{o\ corr}$ = Corrosion Current Density without Inhibitor

I_{corr} = Corrosion Current Density with Inhibitor

Chapter -4

Results & Discussion

In the present study, the behavior of some organic inhibitors containing heteroatom on corrosion of carbon steel (CS) in 1N HCl has been investigated.

The following compounds were selected:

[1]Decanohydrazide (DH)

[2]Dodecnohydrazide (DDH)

[3]Hexadecanohydrazide (HDH)

[4] Octadecanohydrazide (ODH)

The inhibitive action of these above-mentioned compounds on carbon steel is studied by employing two different techniques weight loss and potentiodynamic polarization.

The weight loss measurement were conducted in 1N HCl at different temperatures (30°C, 40° C, 50 °C, 60 °C) using various concentration (100-500 ppm) of the inhibitors and the inhibitors with highest efficiency was also tested for different immersion times (3hr, 6 hr, 9hr,12 hr and 24hr) at optimum concentration (500 ppm) at 30°C .

Polarization experiments were also performed using optimum concentration (500 ppm) of the inhibitors to understand the behaviour of these inhibitors.

4.1 Weight loss studies

The values of percentage inhibition efficiency (%IE) and corrosion rate (CR) obtained from weight loss method at different concentrations of inhibitors at 30°C are summarized in Table 2. It has been found that all these compounds inhibit the corrosion of mild steel in 1N HCl solution, at all concentrations used in this study i.e., 100 – 500 ppm. It has also been observed that the inhibition efficiency for all these compounds increased with the increased in concentrations.

The variation of IE with solution temperature is shown in Fig. 1. It can be seen that IE for all of the compounds cause a significant increase with

an increase in temperature from 30 to 40°C. No significant change in IE has been observed for DH and DDH with the increase of temperature beyond 40-60°C indicating that the inhibitive film formed on the metal surface is protective in nature at higher temperatures. HDH and ODH have been found to show decreasing IE trend for higher temperatures. The decrease in the IE for HDH and ODH may be attributed to decomposition of the hydrophobic long carbon chain at higher temperatures.

The variation of inhibition efficiency of all the four hydrazides with the immersion time is shown in Fig. 2. It is observed that all the tested hydrazides show increase in the inhibition efficiency with the increase of immersion time from 3 to 24 h. This shows the persistency of the adsorbed fatty acid hydrazides over a longer test period.

From Fig. 3, it is clear that IE increases with increase in acid concentration up to 3N HCl for all the hydrazides tested. Further increase in acid concentration up to 5N HCl causes decreased IE for all the hydrazides except for DH. DH having C_9 has shown almost no change in IE with the increase in acid concentration from 3N to 5N HCl.The decrease in IE on increasing acid concentration beyond 3N is due to increased aggressiveness of the acid [87].

4.1.2 Application of Adsorption Isotherm

In order to understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbate on the metal surface must be known. The degree of surface coverage (θ) for different concentration of inhibitors in 1N HCl at 30°C for 3 h of immersion time has been evaluated from weight loss values. The data were tested graphically by fitting to various isotherms. A straight line was obtained on plotting log (θ /1-θ) verses log C. (Fig. 4) suggesting that the adsorption of the compounds from HCl on mild steel surface follows Langmuir's adsorption isotherm.

Inhibition of corrosion of mild steel in the acidic solutions by the oleochemical-based hydrazides can be explained on the basis of molecular adsorption. It is apparent from the molecular structures that

these compounds are able to get adsorbed on the metal surface through π-electrons of aromatic ring and lone pair of electrons of N- and O-atoms, and as a protonated species like amines [88].

The presence of long hydrophobic chain also plays a role in IE by preventing acid solution away from metal surface. Among the compounds investigated in the present study, the order of IE has been found as follows:

$$\underset{(C_{11})}{DDH} > \underset{(C_9)}{DH} > \underset{(C_{15})}{HDH} > \underset{(C_{17})}{ODH}$$

It has been observed that IE of the tested hydrazides increased with the increase in chain length up to C_{11} that's why the IE of DDH is greater than DH but on further increasing carbon atoms more than 11 IE decreased due to increased stearic hindrance to adsorption this lowers IE of HDH and ODH [89].

The values of activation energy (Ea) obtained from Arhenius equation [90,91] and free energy of adsorption (ΔG_{ads}) calculated using the following equations are given in Table 3.

$\Delta G_{ads} = - RT \ln (55.5 K)$

and K is given by:

$K = \theta / C (1 - \theta)$

where θ is degree of coverage on the metal surface, C is concentration of inhibitor in mole /l, K is equilibrium constant, R is a constant and T is temperature. It is found that the ΔG_{ads} value is less than -40 k J/mol (-9.56 k Cal/mol) indicating that the tested hydrazides of fatty acids are physically adsorbed on the metal surface [92]. The low and negative value of ΔG_{ads} indicated the spontaneous adsorption of inhibitor on the surface of mild steel [93]. It was also found that value of activation energy of the inhibited systems were lower than that of uninhibited system. Putilova [94] has indicated that this type of inhibitor is effective at higher temperatures.

Table 2- Corrosion parameters for mild steel in 1N HCl in absence and presence of different concentrations of various inhibitors from weight loss measurement at 30°C for 3 h.

Inhibitor conc.	Weight loss (mg)	IE (%)	CR (mmpy)
Blank1N HCl	60.0	--	22.3
DDH			
100	10.7	82.1	4.0
200	9.7	83.7	3.6
300	8.3	86.1	3.0
400	6.9	88.5	2.5
500	6.4	89.3	2.4
DH			
100	20.3	66.2	7.5
200	15.3	74.5	5.7
300	11.7	80.5	4.3
400	11.2	81.3	4.1
500	9.6	84.0	3.5
HDH			
100	26.2	56.3	9.7
200	22.8	62.0	8.5
300	20.8	65.3	7.7
400	20.2	66.3	7.5
500	19.2	68.0	7.1
ODH			
100	27.3	54.5	10.1
200	24.0	60.0	8.9
300	21.9	63.5	8.1
400	21.6	64.0	8.0
500	21.0	65.0	7.8

Table3- Activation energy (E_a) and free energy (ΔG_{ads}) for mild steel in absence and presence of maximal concentration of the inhibitor.

Inhibitor conc. (ppm)	Ea (Kjmol -1)	ΔG_{ads} (Kjmol -1)			
		30° C	40°C	50°C	60°C
HCl	52.4	-	-	-	-
DDH	86.3	30.7	37.5	37.9	39.9
DH	74.3	29.5	36.7	39.9	39.1
HDH	74.1	26.9	30.8	34.8	33.2
ODH	66.9	27.2	32.4	36.1	32.9

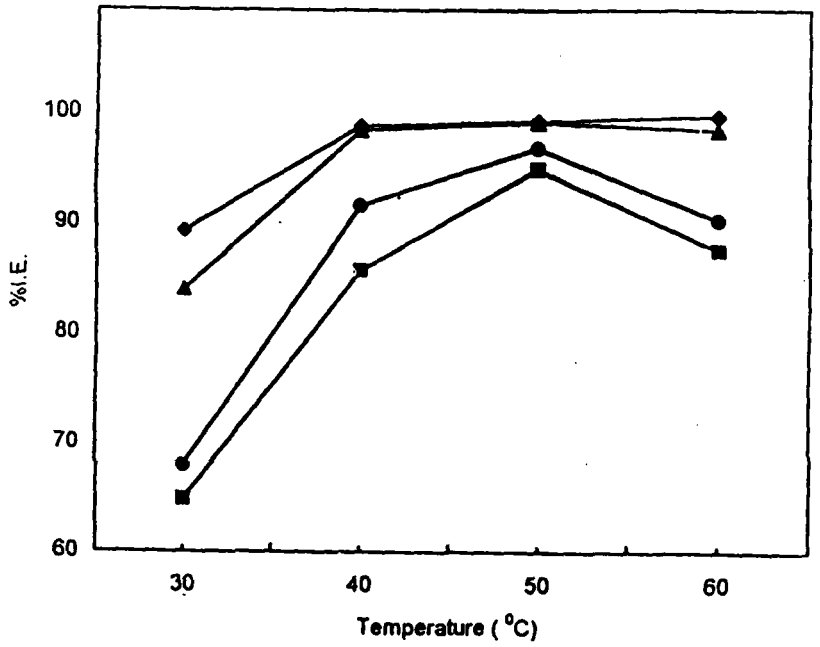


Fig 1- Variation of inhibition efficiency with solution temperature in 1N hydrochloric acid for 500 ppm concentration of inhibitors (♦, DDH; ▲, DH; ●, HDH; ■, ODH).

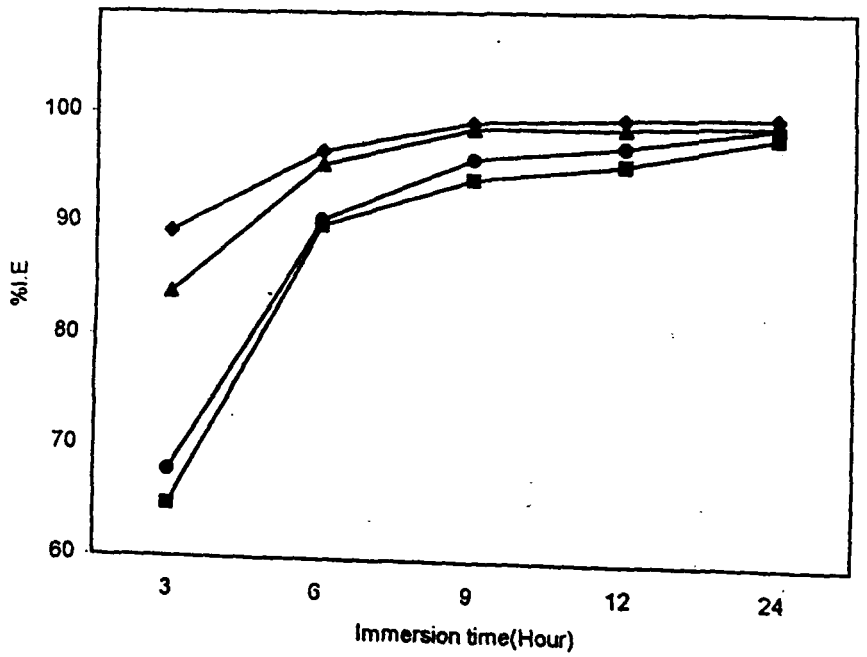


Fig 2- Variation of inhibition efficiency with immersion time in 1N hydrochloric acid for 500 ppm concentration of inhibitors (♦, DDH; ▲, DH; ●, HDH; ■, ODH).

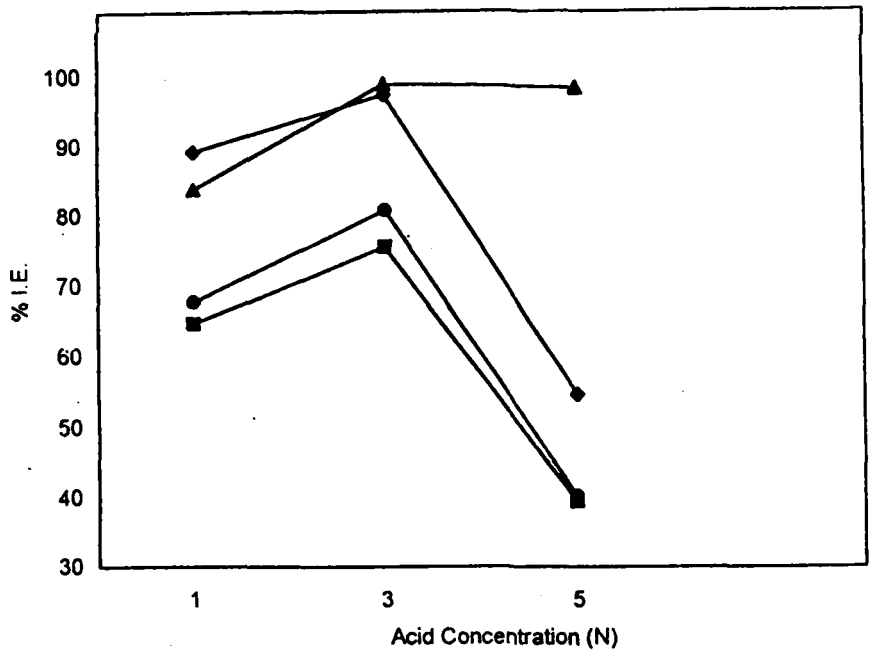


Fig 3- Variation of inhibition efficiency with acid concentration for 500 ppm concentration of inhibitors (♦, DDH; ▲, DH; ●, HDH; ■, ODH).

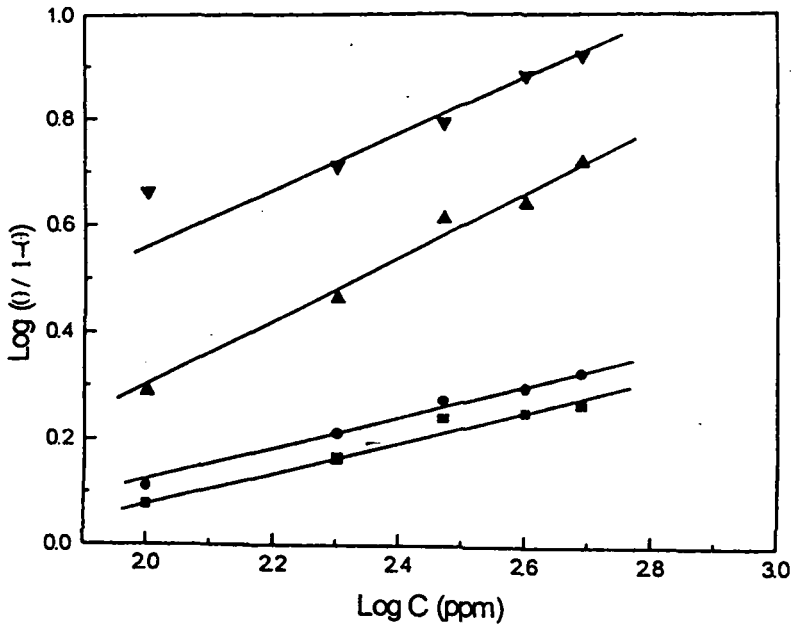


Fig 4- Langmuir s adsorption isotherm plots for the adsorption of various inhibitors in 1N hydrochloric acid on the surface of mild steel (▼, DDH; ▲, DH; ●, HDH; ■, ODH).

4.2 Potentiodynamic Polarization Studies

Various corrosion parameters such as E_{corr}, I_{corr}, IE and CR obtained from Fig. 5 by Tafel extrapolation method are given in Table 4. It is observed that presence of the hydrazides decrease I_{corr} values. Maximum decrease in I_{corr} was observed in case of DDH. The trend of the IE was founds to be same as that of weight loss study. E_{corr} values do not show any significant change in presence of all the hydrazides in the acid solution suggesting that all these hydrazides are mixed type inhibitors (i.e., they retard the corrosion reaction by blocking both anodic and cathodic sites of the metal).

Table 4- Electrochemical polarization parameters for the corrosion of mild steel in hydrochloric acid containing maximal concentration of various inhibitors at 30 °C.

Inhibitor Conc. (ppm)	E_{corr} (mV)	I_{corr} (mA cm^2)	IE (%)	CR (mmpy)
HCl	-458	0.36	-	6.65
DDH	-454	0.08	77.8	1.48
DH	-452	0.11	69.4	2.03
HDH	-456	0.13	63.9	2.40
ODH	-456	0.16	55.5	2.95

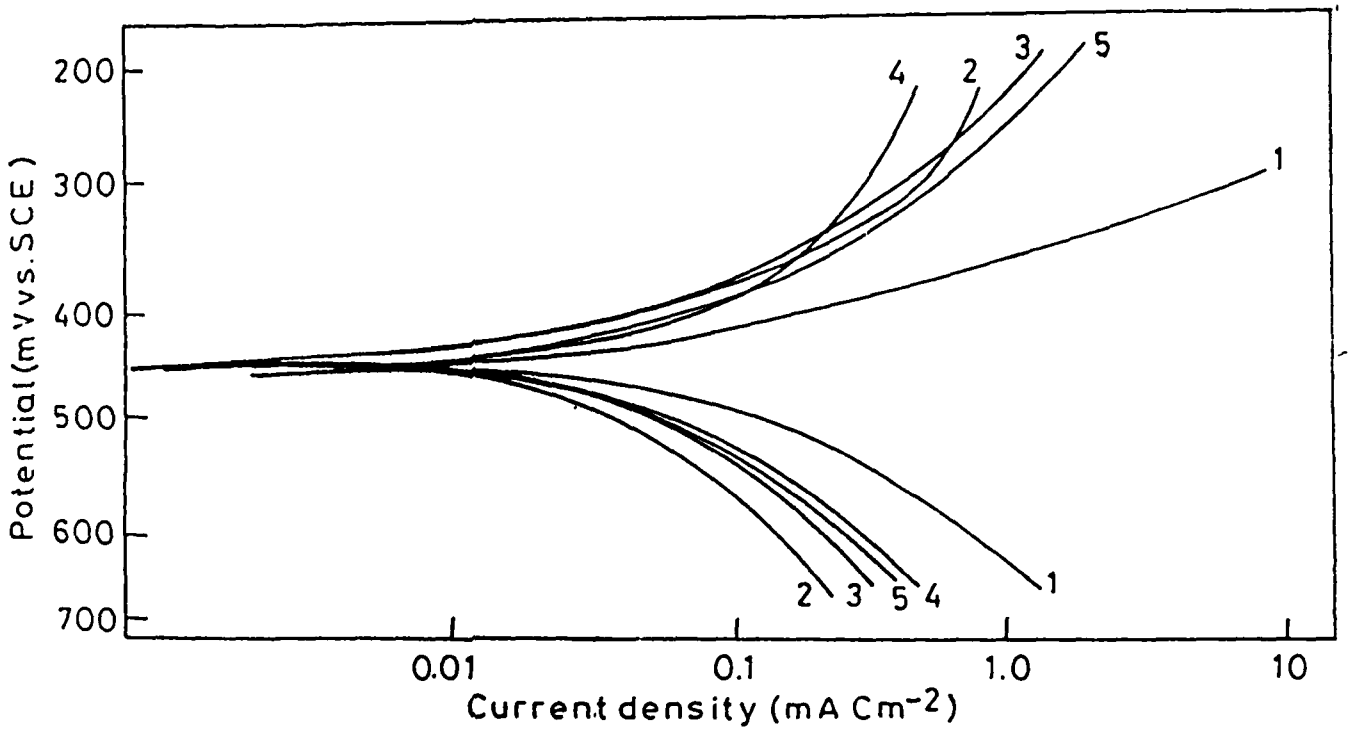


Fig. 5. Potentiodynamic polarization curves of mild steel in 1N hydrochloric acid containing 500 ppm concentrations of various hydrazides (1) Blank (2) DDH (3) DH (4) ODH (5) HDH.

Conclusions

(i) All the Four inhibitors namely,

-Decanohydrazide (DH)

-Dodecanohydrazide (DDH)

-Hexadecanohydrazide (HDH)

-Octadecanohydrazide (ODH)

showed good performance as corrosion inhibitors in 1N hydrochloric acid media for carbon steel from 30°C – 60°C.

(ii) For all the inhibitors, the inhibition efficiency was found to increase with increase in concentrations. All the inhibitors showed their maximum efficiency at 500 ppm.

(iii) All of the four acid hydrazides inhibited corrosion by adsorption mechanism.

(iv) The adsorption of these compounds from acid solution followed Langmuir's adsorption isotherm.

(v) All the compounds examined acted as mixed inhibitors.

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Summary

Corrosion hazard has been increasing day by day and has become a major problem worldwide. Both direct and indirect losses due to corrosion are large and will further increase with industrialization. In USA, the economic losses have been estimated as high as $300 billion per year and in India, the monetary losses due to corrosion have been estimate as high as Rs. 25,000 crores per year.

The most important considerations in any industry today are the reduction in overall costs of the equipments as well as the cost in their production and maintenance. The use of inhibitors has increased manifold during the past several years, due to ease of application and cost effectiveness. But, "one size fit all" philosophy does not work well for corrosion inhibitors. Each inhibitor must tailor to the specific corrosion problem that needs solutions.

Corrosion is the major problem in several industries .It may cause enormous wastage of metallic materials, which leads to heavy economic losses all over the world. In India the monetary losses due to corrosion have been estimated as high as Rs.12000 crores per year.

Among the available methods, of preventing corrosion, the use of inhibitor is one of the most promising methods particularly for closed system. Due to ease of application and cost effectiveness it has attracted a great deal of attention of corrosion scientists and engineers all over the world.

Mild Steel is one of the most important engineering metal, which due to its low cost and excellent mechanical properties, is wildly used as construction material. The mild steel is severely attacked in acid solutions, as usually comes in contact with HCl and H_2SO_4 in various industries, during pickling, cleaning of industrial equipments and acidization of oil wells etc. Inhibited acid solutions are commonly used to reduce the corrosive attack of acid on metals. Use of inhibitor is specific for different systems and thus, it needs to be studied thoroughly.

The worked described in the present dissertation deals with the study of some of oleochemical based hydrazides viz:

Decanohydrazide(DH),Dodecanohydrazied(DDH),Hexadecanohydrazie

(HDH) and Octadecanohydrazide(ODH) on corrosion of mild steel in hydrochloric acid.

The structures of hydrazides selected of investigation are given below:

Table-1 Name and molecular formula of inhibitors

S.N	Inhibitor name	Molecular Structure	M.W	M.P.(°C)
1	Decanohydrazide (DH)	$CH_3\text{-}(CH_2)_8\text{-}C(=O)\text{-}NHNH_2$	186.27	92-95
2	Dodecanohydrazide (DDH)	$CH_3\text{-}(CH_2)_{10}\text{-}C(=O)\text{-}NHNH_2$	214.32	113-14
3	Hexadecanohydrazide (HDH)	$CH_3\text{-}(CH_2)_{14}\text{-}C(=O)\text{-}NHNH2$	270.43	78-79
4	Octadecanohydrazide	$CH_3\text{-}(CH_2)_{16}\text{-}C(=O)\text{-}NHNH_2$	298.48	81-82

The dissertation begins with an introduction along with theoretical background of corrosion highlighting the economical and technological significance of corrosion. Further various theories of corrosion have been described which help in understanding the mechanism of corrosion. Special emphasis has been given to the mode of action of inhibitor towards corrosion prevention. The accounts of various techniques used for investigations of corrosion of inhibitors have also been described briefly.

The apparatus, the description of synthesis of inhibitors and experimental technique adopted such as weight loss and potentiodynamic polarization methods have been described in the experimental section.

The result obtained potentiodynamic and weight loss methods have been discussed in terms of various parameters such as inhibition efficiency, corrosion rate, corrosion current density (I_{corr}) and corrosion

potential (E_{corr}). The influence of concentration of hydrazide on corrosion of mild steel in hydrochloric acid has been studied and optimum concentration of each inhibitor has been evaluated.

The result shows that all the hydrazides inhibit corrosion of mild steel in hydrochloric acid. The inhibition efficiency value of the hydrazides follows the order:

DDH>DH>HDH>ODH

(C_{11}) (C_9) (C_{15}) (C_{17})

The corrosion inhibiting properties of fatty acid hydrazides have been explained in terms of molecular adsorption. It is apparent from the molecular structures that these compounds are able to get adsorbed on the metal surface through π-electrons of aromatic ring and lone pair of electrons of N and O- atoms, and as a protonated species like amines. The presence of long hydrophobic chain also plays a role in IE by preventing acid solution away from metal surface. The excellent performance of DDH is attributed to the presence long hydrophobic chain of C_{11} that's why the IE of DDH is greatest among all the hydrazides as on further increasing carbon atoms more than 11 IE decreased due to increased stearic hindrance to adsorption this lowers IE of HDH and ODH

The results of potentiodynamic polarization studies on mild steel in absence and presence of optimum concentration of hydrazides in HCl clearly bring out the fact that all the compounds under study bring down corrosion current without causing appreciable change in values of corrosion potentials, suggesting that all are mixed inhibitors.

All the compounds are found to follow Langmuir's adsorption isotherm, which implies that the inhibition of mild steel corrosion in HCl occurs through adsorption of hydrazides on mild steel surface.

An interesting feature of the investigation is that all the hydrazides give good performance as corrosion inhibitors in HCl media.